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# Surface Morphology of $(NH_4)_2S_x$-Treated GaAs(100) Investigated by Scanning Tunneling Microscope

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The surface morphologies of n-GaAs(100) after etching with sulfuric acid and sulfur passivation with $(NH_4)_2S_x$ solution were systematically investigated by a scanning tunneling microscope(STM). Depending on the etching and passivation conditions, the surface roughness was observed to be quite different. The effects of water rinse, HCl treatment, and passivation time on the surface morphology were studied through etching and passivation processes. In particular, a very flat surface with a surface undulation of ± 5 Å was obtained after sulfur passivation for 20 min without post-etch water rinse. These studies made a better understanding of a correlation of the routinely used etching and passivation reactions with the surface morphology of GaAs(100) in nanometer scale.

## 1. Introduction

Nanometer scale modification and characterization of passivated semiconductor surfaces is of particular interest for the precise control of ultrafine structures which will be needed to realize the new devices using quantum effects.

Recently, there have been much efforts to passivate GaAs surface with $Na_2S$, $(NH_4)_2S$, or $(NH_4)_2S_x$ solution.[1)-6)] The $(NH_4)_2S_x$ treatments have been proved to be the most effective in reducing surface state densities and surface recombination velocities.[1)-4)] Spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS) and reflection high energy electron diffraction (RHEED) were used to clarify the bonding states in passivation showing that the GaAs surface is S-terminated.[5),6)] Some model calculations were done to explain the surface passivation effect and showed that surface state density was reduced by passivation to result in the movement of Fermi level.[7)]

In order to use the sulfur passivated GaAs surface for the fabrication of ultrafine structures, it is necessary to have a complete understanding of the surface topography before and after the surface treatment. However, systematic studies of surface topography after the routinely used sulfide solution treatment have not been reported yet. In this paper, we tried to understand the effects of etching and sulfur passivation on the surface morphology from the scanning tunneling microscope investigation of chemically treated GaAs(100) surfaces.

## 2. Experiment

The STM used in this experiment was a home-built UHV-STM and calibrated by taking atomically resolved images from the highly oriented pyrolytic graphite and molybdenum disulfide surfaces.[8)] STM tips were prepared by mechanically sharpening the Pt-Ir alloy wire. All STM images were taken in the constant current mode in air and the scanning areas were considerably large, i.e., 3000 Å x 3000 Å. Sample bias voltage, $V_s$, of -4V and the tunneling current, $I_t$, of 1 nA were used in taking STM images from etched and passivated GaAs(100) surfaces.

Samples were n-GaAs(100) wafers with electron concentration of $\sim 10^{18}$ $cm^{-3}$. They were first cleaned by successive treatment with trichloroethane, acetone, alcohol, deionized water, and blown dry in $N_2$ gas. After organic cleaning, the sample was etched by dipping in a room temperature $H_2SO_4 : H_2O_2 : H_2O$ (=7:1:1) solution.

## 3. Results and Discussion

The STM images taken after different sulfuric acid etching time between 30 sec and 5 min showed that surface roughness increased with etching time. Fig. 1 shows the STM image of the GaAs(100) surface after etching for 30 sec and post-etch rinse with flowing deionized water for 10 min. Stable and reproducible images could be observed in successive scans. The surface is covered with randomly distributed island-like features. A line scan through this image gave a surface undulation of ± 19 Å.

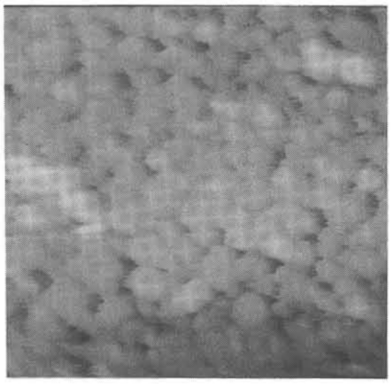

**Fig. 1** STM image taken from the GaAs(100) surface etched with $H_2SO_4$ : $H_2O_2$ : $H_2O$ (=7:1:1) solution for 30 sec and rinsing with flowing deionized water for 10 min. $V_s$ = -4 V, $I_t$ = 1 nA, scanning area = 3080 Å x 2096 Å.

HCl has been used to clean the GaAs sample in the wet process.[5),9)] The effect of HCl treatment on the surface morphology was also investigated in this work. After 30 sec etching and the post-etch water rinse for 10 min, the sample was dipped into the concentrated HCl solution for 10 min and rinsed with deionized water for few sec. As shown in Fig. 2, the surface was smoothed to give the surface undulation of ± 9 Å. All the oxides of arsenic such as $As_2O_3$ and $As_2O_5$ are known to be highly soluble in water. In contrast, gallium oxides are insoluble in water whereas they are slightly soluble in acids.[10)] Therefore, we can expect that HCl treatment for a considerably long time could have removed the residual layers of gallium oxides formed by post-etch water rinse resulting in thinner residual layer and smoother surface.

**Fig. 2** STM image taken from HCl-treated GaAs(100) surface after etching by sulfuric acid solution. $V_s$ = -4 V, $I_t$ = 1 nA, scanning area = 3080 Å x 2096 Å.

Next, surface passivation with $(NH_4)_2S_x$ solution was done after sulfuric acid etching for 30 sec. With variation of surface treatment conditions during etching and sulfur passiavtion, the surface morphology showed dramatic differences.

First of all, the effect of post-etch water rinse on the surface morphology of sulfur-passivated sample was investigated since it is well known that GaAs surfaces slowly dissolve in water. The STM images taken from the sulfur-treated GaAs(100) surfaces by dipping them in the $(NH_4)_2S_x$ solution for 20 min are shown in Fig. 3 and 4. Fig. 3 shows the STM image taken after sulfur passivation with post-etch water rinse for 10 min. As shown in the figure, sulfur passivation after the post-etch water rinse did not improve the surface flatness much compared to that of the as-etched surface. The surface topography was quite similar to that of the unpassivated surface with randomly distributed island-like features. Fig. 4 shows the STM image taken after sulfur passivation without post-etch water rinse. It improved the surface roughness dramatically from the as-etched sample to have the surface undulation of ± 5 Å. It does not show any apparent surface feature.

Such a conspicuous morphological difference shown in Fig. 3 and 4 might be explained by a chemical reaction on GaAs surface. The post-etch rinse with deionized water is known to produce an easily desorbed, gallium-rich amorphous oxide on GaAs.[11)] The gallium-rich oxide is a consequence of the greater solubility of arsenic oxides than that of gallium oxides in water at neutral pH.[12)] Therefore, the post-etch water rinse could cause the changes in the stoichiometry of GaAs to result in the surface roughness.

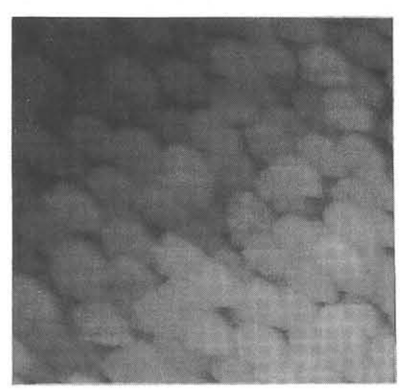

**Fig. 3** STM image taken from the $(NH_4)_2S_x$-treated GaAs(100) surfaces for 20 min with post-etch water rinse for 10 min. $V_s$ = -4 V, $I_t$ = 1 nA, scanning area = 3080 Å x 2096 Å.

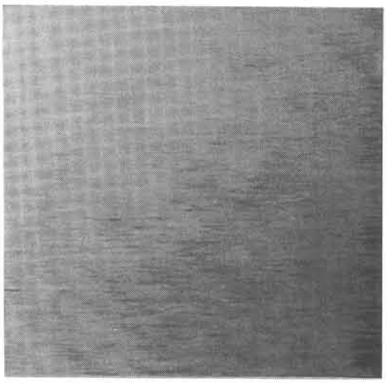

**Fig. 4** STM image taken from the $(NH_4)_2S_x$-treated GaAs(100) surfaces for 20 min without post-etch water rinse. $V_s$ = -4 V, $I_t$ = 1 nA, scanning area = 3080 Å x 2096 Å.

Second, the effect of the passivation time, i.e. dipping time in the $(NH_4)_2S_x$ solution, on the surface morphology was studied. The STM image taken from the sulfur-treated GaAs(100) by dipping it in $(NH_4)_2S_x$ solution for 16 hours showed a very rough surface morphology with peak to trough height of much larger than 100 Å in contrast to that shown in Fig. 4. Such difference can be explained by considering the etching capability of $(NH_4)_2S_x$ solution. $(NH_4)_2S_x$ is known to be able to slowly etch GaAs.[13),14)] A reactive sulfur species, which is known to exist in the $(NH_4)_2S_x$ solution, reacts to etch the GaAs surface. Therefore, the GaAs surface can be oxidized in the $(NH_4)_2S_x$ solution and then the oxide is removed and the oxidation is repeated resulting in the surface roughness.

Third, the effect of subsequent water rinse after sulfur passivation on the surface morphology was examined. After passivation for 20 min, with and without water rinse for 10 min made a big difference in the surface roughness. In contrast to the STM image shown in the Fig.3, where the sample was prepared by subsequent water rinse after etching and passivation, the surface morphology taken from the sample without water rinse after sulfur treatment was very rough and unstable. Such observation can be explained by considering the passivation mechanism of GaAs surface by $(NH_4)_2S_x$ solution. The oxide film on the as-etched surface is removed and the top layer of GaAs is also etched to reveal a fresh GaAs surface. The fresh surface is instantly covered with sulfur, and further precipitation of sulfur might proceed to form an amorphous layer. This deposited amorphous layers are expected to be washed away by water rinse in forms of sulfate $SO_x$ and polysulfur $S_n$ leaving monolayer of sulfur on top of GaAs.[6)] Therefore, there is a possibility that amorphous sulfur layer exists on the sulfur treated GaAs surface to result in the roughness when the sample was not rinsed with water after sulfur treatment.

## 4. Conclusion

The surface morphologies of GaAs(100) after etching with sulfuric acid solution ( $H_2SO_4 : H_2O_2 : H_2O$=7:1:1) and passivation by $(NH_4)_2S_x$ solution were investigated by STM. Depending on the chemical treatments during these processes, the surface roughness was observed to be quite different. The effects of post-etch water rinse, passivation time, and the water rinse after sulfur treatment on the surface morphologies were discussed in terms of the chemical reaction on GaAs surface. In particular, a very flat surface with surface undulation of ± 5 Å was obtained after sulfur passivation by $(NH_4)_2S_x$ solution without post-etch water rinse. These studies made a better understanding of the effect of the routinely used chemical treatments on the surface morphology in nanometer scale.

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